L3 ANSWER 7 OF 20 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 1998:529111 CAPLUS
TITLE: Sensitizer-linked substrates: Rapid delivery of electrons and holes to protein active sites
AUTHOR(S): **Wilker, Jonathan J.**; Dmochowski, Ivan J.; Winkler, Jay R.; Gray, Harry B.; **Dawson, John H.**
CORPORATE SOURCE: Department Chemistry, California Institute Technology, Pasadena, CA, 91125, USA
SOURCE: Book of Abstracts, 216th ACS National Meeting, Boston, August 23-27 (1998), INOR-279. American Chemical Society: Washington, D. C.
CODEN: 66KYA2
DOCUMENT TYPE: Conference; Meeting Abstract
LANGUAGE: English
AB We are developing methods to control enzyme redox states in order to facilitate active intermediate characterization. Photosensitizers such as [Ru(bpy)3]2+ (bpy is 2,2'-bipyridine) are derivatized with hydrocarbon chains terminating in protein substrates. Binding of these sensitizer-substrate conjugates to the protein provides an efficient, covalent pathway for mediating electron transfer between the photosensitizer and the protein active site. Our initial expts. involve the ubiquitous heme oxygenase cytochrome P450cam, [Ru(bpy)3]2+, the protein substrates Et benzene (EB) and adamantane (Ad) as well as the iron ligand imidazole (Im). We describe the synthesis and protein binding properties of Ru-(CH2)11-EB, Ru-(CH2)11-Ad and Ru-(CH2)13-Im. Flash photolysis techniques have been employed to generate strongly oxidizing Ru(III) or reducing Ru(I) derivs. transiently: in these expts., we have succeeded in both oxidizing and reducing the buried heme of P 450cam.

L3 ANSWER 6 OF 20 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 1998:529211 CAPLUS
TITLE: Sensitizer-linked substrates: Delivery of electrons and holes to the active site of cytochrome P450CAM
AUTHOR(S): Dmochowski, Ivan J.; **Wilker, Jonathan J.**; Winkler, Jay R.; Gray, Harry B.; **Dawson, John H.**
CORPORATE SOURCE: Department Chemistry, California Institute Technology, Pasadena, CA, 91125, USA
SOURCE: Book of Abstracts, 216th ACS National Meeting, Boston, August 23-27 (1998), INOR-379. American Chemical Society: Washington, D. C.
CODEN: 66KYA2
DOCUMENT TYPE: Conference; Meeting Abstract
LANGUAGE: English
AB We have developed techniques to rapidly inject electrons and holes into the active site of cytochrome P 450 in an effort to generate and characterize reactive intermediates of this ubiquitous heme oxygenase. Photosensitizers such as [Ru(bpy)3]2+ (bpy is 2,2'-bipyridine) are covalently attached to hydrocarbon chains terminating in protein substrates. Binding of these sensitizer-linked substrates creates a direct, covalent pathway that mediates efficient electron transfer (ET) between the ruthenium and the heme. Initial expts. involve the Ru-tethered protein substrates Et benzene (Ru-(CH2)11-EB) and adamantane (Ru-(CH2)11-Ad), as well as the ligand imidazole (Ru-(CH2)13-Im). We describe the synthesis and protein binding of these sensitizer-substrate conjugates. Laser photoexcitation of the sensitizer, followed by oxidative or reductive quenching of the excited state, generates oxidizing Ru(III) or reducing "Ru(I)" derivs. transiently. By these rapid, active-site-directed methods, we have demonstrated the oxidation and reduction of the cytochrome P 450 heme to states unobserved previously.

L3 ANSWER 5 OF 20 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 1999:92288 CAPLUS
TITLE: Sensitizer-linked substrates: Complexes for the rapid generation of reduced and oxidized enzyme states
AUTHOR(S): **Wilker, Jonathan J.**; Dmochowski, Ivan J.; **Dawson, John H.**; Winkler, Jay R.; Gray, Harry B.
CORPORATE SOURCE: Department of Chemistry, California Institute of Technology, Pasadena, CA, 91125, USA
SOURCE: Book of Abstracts, 217th ACS National Meeting, Anaheim, Calif., March 21-25 (1999), INOR-471. American Chemical Society: Washington, D. C.
CODEN: 67GHA6
DOCUMENT TYPE: Conference; Meeting Abstract
LANGUAGE: English
AB We are developing techniques to generate and observe fleeting enzyme intermediates in buried active sites. The design and synthesis of conjugates linking protein substrates and photoaddressable redox agents will be described. Protein binding of the substrate moiety creates a covalent pathway to mediate efficient electron and hole transfer between the [Ru(bpy)3]n+ (bpy is 2,2'-bipyridine) photosensitizer and enzyme active site. By applying this strategy of linking protein substrates and photosensitizers, we show the heme of cytochrome P 450cam in two redox states unobserved previously: the ferrous aquo, (P)Fe2+-OH2, and the ferric aquo porphyrin cation radical, (P+)Fe3+-OH2.